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R. M. Joshi[a]
[a] National Chemical Laboratory, Poona, India

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A Brief Survey of Methods of Calculating Monomer Reactivity Ratios*

R. M. JOSHI

National Chemical Laboratory
Poona, India

ABSTRACT

Various published methods of calculating monomer reactivity ratios are surveyed in the light of computer analysis of a large number of experimental data. One typical system, vinyl chloride-methyl acrylate, is discussed in detail. Some of the earlier methods, such as the Fineman-Ross method and the graphical Mayo-Lewis solution, are considered obsolete. The most preferred method for kinetic interpretations of copolymerization data is indicated.

INTRODUCTION

Since the publication of the new analytical solution [1] to the Mayo-Lewis plot of the linear form of copolymer composition equation, we have analyzed a large number of experimental systems by this and many other existing methods, using appropriate computer programs made for both differential and integral forms of the equation. Results

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obtained for one typical system, vinyl chloride (M_1) and methyl acrylate (M_2), using experimental data of Chapin, Ham, and Fordyce [2] are given in Table 1 which illustrate the diversity in numerical values of monomer reactivity ratios (MRR) given by different methods for one and the same experimental datum. The efficacy of different methods in obtaining a maximum likelihood estimate of the MRR parameters for this system are discussed and the most preferred procedure to be adopted for future copolymerization studies is indicated.

SUMMARY OF METHODS

The main features of various published methods under this survey are summarized below.

The JJ Method [1]. This most recently published procedure has eliminated the subjective element in the selection of the "best" point of intersection on the Mayo-Lewis plot, which is "statistically" the closest point to all experimental lines. Its coordinates are calculated without actually drawing the Mayo-Lewis plot. The analytical solution of the coordinates of the point of intersection is a weighted, linear, least-squares solution with $1/1 + m_i^2$ ($= \cos^2 \vartheta$, where ϑ is the angle of inclination of the line) as the weighting factor. The method is simple to operate manually without the aid of a computer, at least for the differential form of the composition equation.

The method has since been extended to the integral equation with the following procedure. A first rough estimate of MRR is obtained using the differential equation and average mole-fractions of monomer feed, from which the region of intersection is located for the purpose of fixing the ranges of "p," an auxiliary constant of the integral equation. For each integral curve, p is fixed automatically by an auxiliary analytical manipulation (covered by Eqs. A-20 to A-23 of the complete computer program schedule given in the Appendix) so that an appropriate portion of the integral curve is fixed which is later approximated as the root mean square (rms) straight line and its slope and intercept computed by Eqs. (A-24) to (A-28) in the Appendix. The new slopes and intercepts are treated in the same manner as for the differential equation procedure. In the several hundreds of systems analyzed thus, it has been firmly established that the slopes and intercepts calculated by making use of the simple arithmetic average of initial and final monomer feeds in the differential equation tally very closely with those from the approximated integral curves, at least to two digits, and the corresponding MRR values agreeing to three digits or better. This is an important observation which the author would like to reemphasize [3]. Thus when

TABLE 1. Comparison of MRR Values Computed by Various Procedures for the System Vinyl Chloride (M_1)-Methyl Acrylate (M_2), Taken from the Work of Chapin, Ham, and Fordyce [2]

Method and procedure		Reported value [2]	FR method [9] (slopes)	JK method [4] (tan θ)	JJ method [1]	YBR method [8]	TM method [10]
A Differential equation (ignoring conversion, WFC = 0)	r_1	0.083	0.0827	0.0637	0.0590	0.0744	0.0909
	r_2	9.0	8.9290	9.0605	8.9874	9.0598	10.0655
Error ($10^4 \times \Sigma d^2$)		36.04	36.04	43.19	49.24	37.17	31.07
B Differential equation (using average feed ratios)	r_1		0.0766		0.0500	0.0670	0.090[a]
	r_2		9.1293		9.1848	9.2737	11.0[a]
C Integrated equation (linearizing the integral curves)	r_1		-		0.0498	0.0669	
	r_2		-		9.1818	9.2707	

[a]Calculated by this author.

conversions are restricted to 10 or even up to 20%, the laborious calculations of the integral equation are quite unnecessary to obtain the final values of the MRR computed without exceeding the inherent experimental errors involved in copolymerization work.

The JK Method [4]. This method, published in 1955 with a view to eliminating subjective error in the location of the best point on the Mayo-Lewis plot and obtaining some quantitative estimate of the standard deviation, considers all $n(n - 1)/2$ intersections of pair-combinations of n experimental lines. The weighting factor is either $\tan \phi$, $\sin \phi$ [5], or $\tan \phi/2$ (unpublished) where ϕ is the angle of intersection of the two lines. These weighting factors are all empirical with no physical significance attributable to the best point derived. They only denote how far-removed are the two experiments on the monomer composition axis and how much range of the monomer feed is covered. Flat intersections of any two close experiments are automatically eliminated from the average due to the vanishingly small angle of intersection, and conversly, wide-angle intersections are weighted heavily. This method was extended to integral equation by Shtraikhman [6] and has also been employed occasionally in some early computer programs for deriving MRR [7].

The YBR Method [8]. Yezrielev, Brokhina, and Roskin transformed the linear equation of copolymer composition into the symmetrical form

$$F/f^{\frac{1}{2}} \cdot r_1 - f^{\frac{1}{2}}/F \cdot r_2 + (1/f^{\frac{1}{2}} - f^{\frac{1}{2}}) = 0 \tag{1}$$

where $F = M_1/M_2$ and $f = m_1/m_2$. This equation retains the same form on inversion of the datum, i.e., F and f changing to 1/F and 1/f, respectively, when monomer order is reversed. Hence a unique solution results from both normal and inverted data as in the JJ method. The least squares solution for the parameters of the straight line represented by the above equation have formulas different from those of the slope-intercept form in the well-known method of Fineman and Ross [9]. These are given below in terms of the familiar quantities, the slope $m = F^2/f$ and the intercept $c = F(1/f - 1)$ on the r_2 vs r_1 plot.

$$r_1^0 = \frac{ND - BC}{AC - N^2} = \left[\frac{\Delta^2 C}{AC - N^2}\right]^{\frac{1}{2}} \tag{2}$$

$$r_2^0 = \frac{AD - NB}{AC - N^2} = \left[\frac{\Delta^2 A}{AC - N^2}\right]^{\frac{1}{2}} \tag{3}$$

where $A = \sum^{N} m_i$, $B = \sum^{N} c_i$, $C = \sum^{N} 1/m_i$, $D = \sum^{N} c_i/m_i$, N = number of experiments, and Δ = the rms error as given by

$$\Delta = \left[\frac{\sum^{N} \Delta_i^2}{N-2}\right]^{\frac{1}{2}} \quad (4)$$

where $\Delta_i = (r_1{}^{o} m_i + c_i - r_2{}^{o})$.

We extended the above formulas to the integrated equation through the same auxiliary analytical technique (as used for the JJ method) of automatic selection of the parameter p to cover the significant region, treating the integral curves as rms straight lines and computing the new slopes and intercepts in Eqs. (2), (3), and (4). The complete set of equations for our computer program of the YBR method is given in the Appendix.

TM Method [10]. Tidwell and Mortimer adopt a nonlinear least-squares procedures, different from all the previous linear methods, by fitting the experimental mole-fractions m_2 ($= m_2/m_1 + m_2$) of the copolymer to the theoretical curve in the form due to Skeist [11], m_2 vs M_2. The theoretical curves are computed on the basis of an initial rough estimate of r_1 and r_2, and its refinement is made by successive iterations so as to minimize the sum of mean-square deviation, Σd^2, of the experimental points from the theoretical curve. This is done more or less by the standard Gauss-Newton nonlinear least-squares procedure with modifications [12] which ensure and expedite convergence in the process of iteration. Generally two or three iterations are adequate for the copolymerization data. The TM method presumes that there is no possible experimental error in the independent variable, i.e., M_2, or the monomer composition of the feed, and that the absolute error in m_2 (copolymer composition) is independent of its value, or constant. The method has been claimed [13] to be the best procedure so far evolved to compute the MRR and their confidence region, and recommends that only a certain range of monomer feed (generally that would result into a copolymer with 30 to 70% m_2) leads to maximum reliable information about the MRR of a copolymerization system.

FR Method [9]. Fineman and Ross were the first to arrange the differential copolymer composition equation in the following linear form:

$$F\,(1 - 1/f) = -(F^2/f)r_1 + r_2 \quad (5)$$

where $F = M_1/M_2$ and $f = m_1/m_2$. If one graphs $F(1 - 1/f)$ vs $-F^2/f$, the slope of the straight line is r_1 and the intercept is r_2. The method has received much acceptance in copolymerization literature although it gives two different solutions for the same experimental datum when the monomer sequence is reversed, the values derived from slope nonetheless being taken as the MRR values. This method has now been totally replaced by the YBR method, at least in principle.

DISCUSSION

Table 1 presents the MRR values for the system vinyl chloride (M_1)-methyl acrylate (M_2), obtained through the different methods under review. There are two distinct objectives in the process of evaluating the MRR values with precision for any copolymerization system; 1) prediction of copolymer composition for any starting feed, and 2) understanding the kinetic features of copolymerization implied in the relative reactivities of the propagating free radical with the two monomers ($r_1 = k_{11}/k_{12}$; $r_2 = k_{22}/k_{21}$). The obvious criterion for 1) is a good fit of experimental points with the theoretical curve of copolymer composition vs monomer feed. This criterion is directly followed by the TM method which is a computerized curve-fitting method, but less directly by other methods such as the JJ method or the YBR method where some other functions of the two variables are fitted best by the least-squares procedure. The Σd^2 value in Table 1 is a direct measure of the efficacy of a computation method in predicting the copolymer composition. Apparently the TM method is the best method in this regard, provided that the absence of a multiple minima in every case is ensured by the computation technique. For this particular system, values given by the original authors [2] by graphical curve-fitting and personal judgement, and even the FR solution (from slopes only), score high in minimizing the Σd^2. This is, however, fortuitous. From our analysis of a large number of other experimental data we observe that more often irrational solutions with very high Σd^2 result from graphical methods and from the FR method. This applies equally well to the JK method which uses empirical weighting factors. Our recently published JJ method was also found to be hopelessly inaccurate in fulfilling the objective of minimizing Σd^2, which is achieved fully in the TM method. It also gives negative MRR values for apparently good experimental data [14]. On the other hand, the YBR method, which now rationally replaces the FR method by virtue of its ability to yield a unique solution from normal and inverted datum due to an ingeneous manipulation of the same linear equation of the FR method, was found to be next-best to the TM method in attaining the minimum of Σd^2.

The criterion of minimum Σd^2 achieved in the TM method may not, however, always coincide with the attainment of the best MRR values that will truly represent these parameters kinetically for the particular system. A few erratic experimental points will carry the MRR values astray in the process of minimizing Σd^2. The TM method needs some reexamination as regards its ability to circumvent an occasional erratic experiment in the set of experimental data. Figure 1 shows the theoretical curve drawn with TM values of MRR taken from Table 1, together with experimental points 1 through 8. It is readily seen that experimental point 2 is slightly "off" in this set. The TM procedure, in an attempt to negotiate with this point to minimize Σd^2, has indirectly led to the suggestion that there is a systematic, negative error in composition analysis (high percent chlorine) in 6 out of the 8 experiments (i.e., points 1,3,4,5,6 and 8) which fall below the TM curve throughout. The theoretical TM curve does not look like a good fit since it only passes "near enough to" but not through the experimental points, and no experimenter may readily accept it. A better and rational curve-fitting seems to be achieved by the YBR method as shown in Fig. 2. Here the curve passes evenly between the experimental points, with three points above the curve four points below the curve, with one point almost on the curve. The MRR values given by the YBR method have a slightly higher Σd^2 than the TM method, but may actually be a better estimation of the ambient kinetic parameters (k_{11}, k_{12}, etc.) prevailing over the entire copolymerization range since the YBR curve is not deflected much by one stray experimental point, No. 2.

The characteristic and basic deficiency in the TM computational procedure appears to be the fact that it minimizes the sum of squares of the vertical distances, "d," in Fig. 1, i.e., the error element on the copolymer composition axis only. It presumes that there is no error present in the monomer-feed composition, the independent variable. This may not be the case with all experimental data in the literature, especially more recent work where the initial and final monomer compositions are independently estimated, for instance, by gas-liquid chromatography, as in the work of Johnston and Rudin [15] or German and Heikens [16]. For the purpose of a general method of computing MRR, it would be more reasonable to assume that the experimental error can occur in both monomer feed and in the copolymer composition, in which case the normal distance "b" in Fig. 1, rather than the distance "d," should be the one to be minimized by the least-squares procedure. Due to the complexity of the equation of the copolymer composition curve, an absolute mathematical solution for the minima of Σb^2 is not possible without linearizing the equation as in the JJ method or the YBR method. But an iterative computer program similar to the TM method may be feasible. Such efforts are under way. It is yet to be seen whether the solution of this kind of nonlinear iterative scheme will coincide with any of the linear equation methods, particularly the YBR method which may be accepted as the best linear method.

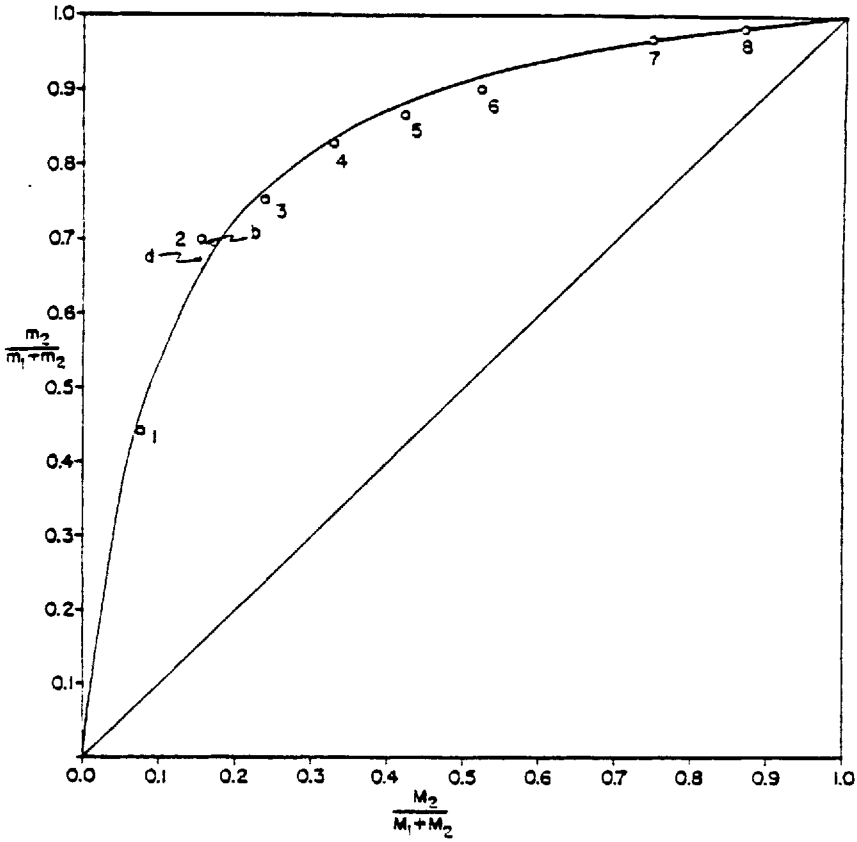

FIG. 1. Experimental data of Chapin et al. [2] for the system vinyl chloride (M_1)-methyl acrylate (M_2) and the best-fitted theoretical curve of Tidwell and Mortimer [10].

CONCLUSIONS

The following conclusions are made on the basis of experience gained by handling several hundreds of copolymerization systems but signified merely by one system cited and discussed above.

1. Some of the earlier methods of computation of monomer reactivity ratios have now become obsolete and should not be propagated in the copolymerization literature. These include the empirical JK method, the graphical Mayo-Lewis solution, and the FR method.

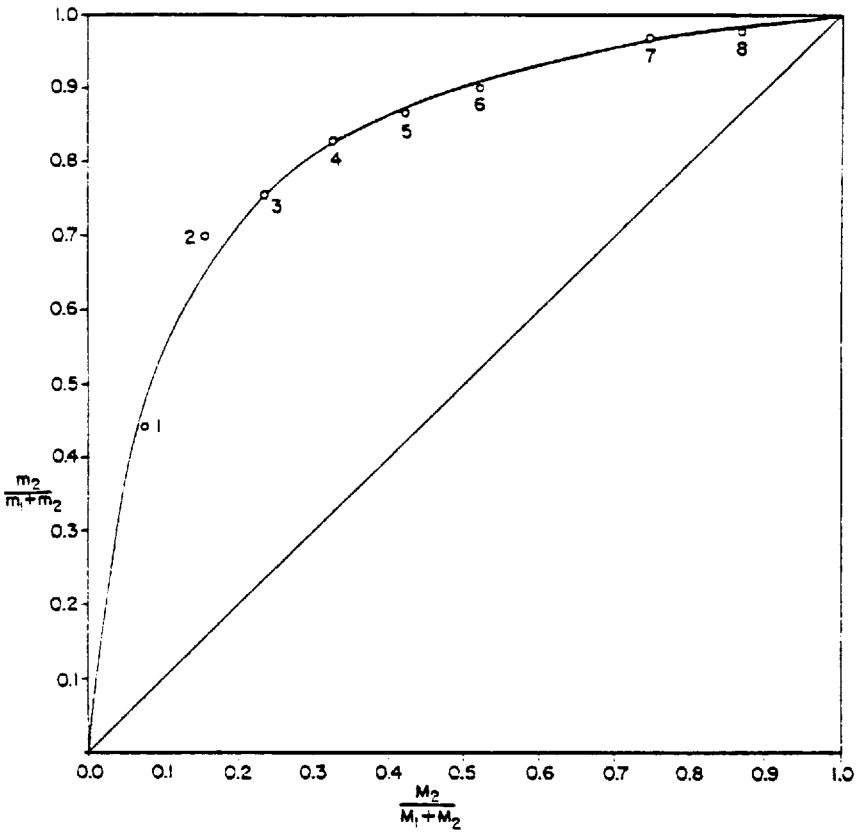

FIG. 2. Experimental data of Chapin et al. [2] for the system vinyl chloride (M_1)-methyl acrylate (M_2) and the best-fitted theoretical curve of Yezrielev et al. [8].

2. The FR method has been completely and most satisfactorily replaced by the YBR method.

3. The graphical Mayo-Lewis treatment and the subjective selection of values is thoroughly replaced by the JJ method. However, the method has been found to be unsatisfactory in yielding a rational solution, perhaps a limitation of the Mayo-Lewis plot itself.

4. The two outstanding present day methods are the nonlinear TM method and the linear YBR method. While the former is most accurate in matching copolymer composition, the YBR method gives a very balanced average in spite of any stray experimental error in a set of data.

5. If conversion in copolymerization experiments is kept within 10 to 20%, the use of average monomer feed ratios and the differential equation can be safely adopted in place of the laborious procedure of the integrated equation, without causing any loss of accuracy beyond inherent experimental error.

6. An important property of the YBR method has been noted. While the YBR theoretical line represents the least-squares line for the plot of linear, symmetrical Eq. (1), covering both normal and the inverted datum, it also represents a line which is found to fulfill exactly the condition: $\Sigma(ER)_i = 0$ (in Eq. A31 of the Appendix). This ensures that the YBR line is situated evenly between the experimental points of positive and negative error, $\overline{\pm(ER)}_i$. This is a very desirable feature of the YBR solution, unattained in other linear methods so far developed.

APPENDIX

Glossary of Symbols

a = molecular weight of Monomer 1

b = molecular weight of Monomer 2

M_2^0 = initial mole-fraction of Monomer 2 in the feed

$\overline{m}_2$ = average mole-fraction of Monomer 2 in the copolymer composition

WFC = weight-fraction conversion

MFC = mole-fraction conversion

N = number of observations/experiments

$\overline{M}_2$ = mean mole-fraction of Monomer 2 in the feed

M_1, M_2 = final mole-fractions of monomers after conversion WFC

m_i = slope ($\tan \theta_i$) of the i-th experimental line on the r_2 vs r_1 (Mayo-Lewis) plot

c_i = intercept of the above line on the r_2 axis

α_i = $\cos \theta_i$, $\beta_i = \sin \theta_i$: auxiliary functions of the inclination angle of the i-th line, used for confining an appropriate portion of this line in the region of intersection.

$(r_1)_i$, $(r_2)_i$ = coordinates of the point of intersection of the normal from the "best" point (r_1^0, r_2^0), and the i-th line

(r_1^0, r_2^0) = coordinates of the "best" point of intersection treating the differential equation by the YBR method [8], or the JJ method [1] for its corresponding computer program

P_i^j = arbitrary parameter of the integrated equation of copolymer composition, as defined by Eq. (A-20).

Z = auxiliary constant controlling the range of P_i^j in Eq. (A-20). A value of 0.1 for this constant is generally suitable for most systems

$(r_1)_i^j$, $(r_2)_i^j$ = arbitrary coordinates of the j-th point around the i-th line drawn on the basis of the differential equation, and used for the purpose of computing P_i^j only

$(R_1)_i^j$, $(R_2)_i^j$ = absolute coordinates of the j-th point on the i-th integral curve

x_i = slope of the i-th rms line passing through the three arbitrary points represented by $(R_1)_i^j$, $(R_2)_i^j$

y_i = intercept of the above rms line on the r_2 axis

R_1^o, R_2^o = the final MRR values from the integrated equation

S, or s = symbols for the standard deviations of MRR values from the integrated and differential equations, respectively

$(ER)_i$ = error in individual experiment with respect to the best fit by the YBR method [8]

Schedule of Equations for Computer Programs

Input Data

a, b, M_2^o, $\overline{m}_2$, WFC, and Z (= 0.1, generally)

Computation of Slopes (m_i) and Intercepts (c_i) for Differential Equation Procedure

$$MFC = WFC \frac{M_2^o b + a(1 - M_2^o)}{\overline{m}_2 b + a(1 - \overline{m}_2)} \tag{A-1}$$

$$\overline{M}_2 = \frac{2 M_2^o - MFC (M_2^o + m_2)}{2(1 - MFC)} \tag{A-2}$$

$$F = (1/\overline{M}_2) - 1 \tag{A-3}$$

$$f = (1/\overline{m}_2) - 1 \tag{A-4}$$

$$m_i = F^2/f, \; i = 1, 2, 3, \ldots, N \tag{A-5}$$

$$c_i = F\,(1/f - 1), \; i = 1, 2, 3, \ldots, N \tag{A-6}$$

Computation of rms Slopes (x_i) and Intercepts (y_i) for the Integrated Equation Procedure

$$r_1{}^0 = \frac{N\,\Sigma\, c_i/m_i - \Sigma\, c_i \cdot \Sigma\, 1/m_i}{\Sigma\, m_i \cdot \Sigma\, 1/m_i - N^2}, \; \Sigma = \sum_{i=1}^{N} \tag{A-7}$$

$$r_2{}^0 = \frac{\Sigma\, m_i \cdot \Sigma\, c_i/m_i - N\,\Sigma\, c_i}{\Sigma\, m_i \cdot \Sigma\, 1/m_i - N^2}, \quad \Sigma = \sum_{i=1}^{N} \tag{A-8}$$

For JJ method program, Eqs. (2) and (3) of Ref. 1 replace Eqs. (A-7) and (A-8) above.

$$(r_1)_i = \alpha_i{}^2(r_1{}^0 + m_i r_2{}^0 - m_i c_i) \tag{A-9}$$

$$(r_2)_i = m_i (r_1)_i + c_i \tag{A-10}$$

$$\alpha_i = (1/1 + m_i{}^2)^{\frac{1}{2}} = \cos\vartheta_i \tag{A-11}$$

$$\beta_i = (m_i{}^2/1 + m_i{}^2)^{\frac{1}{2}} = \sin\vartheta_i \tag{A-12}$$

$$M_2 = M_2{}^0 - MFC(\overline{m}_2) \tag{A-13}$$

$$M_1 = (1 - M_2{}^0) - MFC(1 - \overline{m}_2) \tag{A-14}$$

$$M_1{}^0 = 1 - M_2{}^0 \tag{A-15}$$

$$B = M_1{}^0/M_1 \tag{A-16}$$

$$C = M_2{}^0/M_2 \tag{A-17}$$

$$D = M_1^0/M_2^0 \tag{A-18}$$

$$E = M_1/M_2 \tag{A-19}$$

$$P_i^j = \frac{1 - (r_1)_i^{j=i,+d,-d}}{1 - (r_2)_i^{j=i,+d,-d}} \qquad (J = 3) \tag{A-20}$$

$$(r_1)_i^{j=i} = (r_1)_i;\ (r_2)_i^{j=i} = (r_2)_i \tag{A-21}$$

$$(r_1)_i^{j=\pm d} = (r_1)_i(1 \pm \alpha_i Z) \tag{A-22}$$

$$(r_2)_i^{j=\pm d} = (r_2)_i(1 \pm \beta_i Z) \tag{A-23}$$

$$A_i^j = \frac{1 - E(P_i^j)}{1 - D(P_i^j)} \tag{A-24}$$

$$(R_2)_i^j = \frac{\log C - 1/P_i^j(\log A_i^j)}{\log B + \log A_i^j} \tag{A-25}$$

$$(R_1)_i^j = 1 - P_i^j(1 - (R_2)_i^j) \tag{A-26}$$

$$x_i = \frac{\Sigma(R_1)_i^j \cdot \Sigma(R_2)_i^j - 3\,\Sigma(R_1)_i^j\,(R_2)_i^j}{(\Sigma(R_1)_i^j)^2 - 3\,\Sigma((R_1)_i^j)^2},\quad \Sigma = \sum^{J=3} \tag{A-27}$$

$$y_i = \frac{\Sigma(R_1)_i^j \cdot \Sigma(R_1)_i^j(R_2)_i^j - \Sigma((R_1)_i^j)^2 \cdot \Sigma(R_2)_i^j}{(\Sigma(R_1)_i^j)^2 - 3\,\Sigma((R_1)_i^j)^2},\quad \Sigma = \sum^{J=3} \tag{A-28}$$

Subroutine for the YBR Method [8]

Differential equation:

$$r_1^{0} = \text{repeat Eq. (A-7)} \tag{A-29}$$

$$r_2^{0} = \text{repeat Eq. (A-8)} \tag{A-30}$$

$$(ER)_i = m_i r_1^{0} - r_2^{0} + c_i \tag{A-31}$$

$$(ER)^{0} = (\Sigma (ER)_i^{2}/(N - 2))^{\frac{1}{2}} \tag{A-32}$$

$$s_1 = \pm (ER)^{0}\left[\frac{\Sigma 1/m_i}{\Sigma m_i \cdot \Sigma 1/m_i - N^2}\right]^{\frac{1}{2}} \tag{A-33}$$

$$s_2 = \pm (ER)^{0}\left[\frac{\Sigma m_i}{\Sigma m_i \cdot \Sigma 1/m_i - N^2}\right]^{\frac{1}{2}} \tag{A-34}$$

For JJ program, Eqs. (A-31) to (A-34) are replaced by Eqs. (6) and (7) of Ref. 1.

Integrated equation:

To obtain R_1^{0}, R_2^{0}; the final MRR values; and their standard deviations S_1 and S_2; repeat the above subroutine putting $m_i = x_i$ and $c_i = y_i$.

Note: The subscript i for Eqs. (A-1) to (A-4) and (A-13) to (A-19) has been omitted for convenience.

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